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FEATURE ARTICLE

Tetracyanoethylene-based organic magnets

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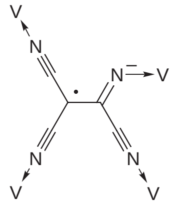
Several classes of organic magnets based upon the tetracyanoethenide radical anion, [TCNE]$^{\cdot-}$, either unbound, μ, and μ_4 bonded to zero, two and four metal sites have been reported. The putative μ_4 bonded V(TCNE)$_x$ room temperature magnet has been extended to include M(TCNE)$_x$ (M = Mn, Fe, Co, Ni) magnets. M for this class of magnets is assigned to be in the divalent oxidation state. A σ-[TCNE]$_2^{2-}$ dimer intermediate has been isolated. The intrachain magnetic coupling for the 1-D coordination polymers having [TCNE]$^{\cdot-}$ μ-bridge bonded to [Mn$^{\rm III}$porphyrins]$^+$ is discussed in the context of a structure–function correlation arising from the dihedral angle between the [Mn$^{\rm III}$TPP]$^+$'s MnN$_4$ and [TCNE]$^{\cdot-}$ mean planes and the magnitude of magnetic coupling. This correlation is ascribed to the increasing importance of the σ-Mn$^{\rm III}$ d$_{z^2}$/[TCNE]$^{\cdot-}$ p$_z$ overlap with decreasing dihedral angle.

From time immemorial magnets comprised a few metals or their oxides with the key component of all magnets, the unpaired electron spins, solely residing in d- or f-orbitals. Extension to organic radicals was first discussed in 1963 from a conceptional point of view,[1] but their experimental realization was not achieved until 1985. At that time [Fe(C$_5$Me$_5$)$_2$]$^{\cdot+}$[TCNE]$^{\cdot-}$ (TCNE = tetracyanoethylene) with a magnetic ordering temperature, T_c, of 4.8 K was reported to be the first magnet with spin residing in a p-orbital[2] that (i) required spins in p-orbitals, (ii) exhibited magnetic hysteresis, (iii) did not have extended network bonding in 1, 2 or 3 dimensions, (iv) was soluble in conventional organic solvents, and (v) did not require metallurgical preparative methods. Today, molecule-based magnets include many diverse examples of materials exhibiting magnetic ordering including ferromagnets, ferrimagnets, canted/weak ferromagnets, metamagnets and spin glasses. Materials range from p-orbital-based organic nitroxides,[3,4] p/d-orbital-based mixed organic radicals/organometallic or inorganic coordination systems,[4–6] to the more classical d-orbital-based inorganic coordination compounds (*e.g.* mixed metal oxalates and cyanides),[4,5] with several classes of the organic/metal-ion-containing-ones possessing TCNE studied in our laboratory. As is the intent of feature articles in this journal, we provide a personal account of the results on two classes of TCNE-based magnets, namely, M[TCNE]$_x$ and [Mn(porphyrin)][TCNE] magnets. Broad reviews on molecule-based magnets, however, are available.[3–6]

M(TCNE)$_x$ Magnets

In 1991 V(TCNE)$_x\cdot y$(CH$_2$Cl$_2$) (x ~ 2; y ~ 1/2) **1a**, prepared from the room temperature reaction of V^0(C$_6$H$_6$)$_2$ and TCNE, was reported to be a magnet below a critical temperature estimated to be ~400 K.[4,7] Owing to the structural disorder, variable composition and extreme oxygen/water sensitivity the structure and oxidation state assignment of this valence-ambiguous material has yet to be elucidated. Although the structure is as yet unknown, based upon the magnetic, IR, and elemental analyses data, **1a** is formulated as V$^{\rm II}$(TCNE)$_2\cdot$1/2(CH$_2$Cl$_2$) with S = 3/2 V$^{\rm II}$ and two S = 1/2 [TCNE]$^{\cdot-}$ systems. A 3-D network structure **2**, with each vanadium surrounded by up to six ligands which are primarily nitrogens from different [TCNE]$^{\cdot-}$ species, and the [TCNE]$^{\cdot-}$ species binding up to four different vanadiums *via* σ-N bonds, is proposed.



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Compound **1a** exhibits a field-dependent magnetization, $M(H)$, between 1.4 and 350 K (Fig. 1), and saturates to *ca.* 6 × 10^3 emu Oe mol^{-1} at 2 K and 19.5 kG. Assuming a Landé g value of 2, the expected maximum or saturation magnetization, M_s, for ferromagnetic coupling between S = 3/2 V$^{\rm II}$ and the two S = 1/2 [TCNE]$^{\cdot-}$ species (*ie.* $S_{\rm total}$ = 5/2) is 28 × 10^3 emu Oe mol^{-1}. In contrast, antiferromagnetic coupling, leading to ferrimagnetic behavior as observed for magnetite (Fe$_3$O$_4$), leads to an $S_{\rm total}$ of 1/2 with M_s expected to be 5.6 × 10^3 emu Oe mol^{-1}. The latter is in good agreement with the observed value. Hysteresis, characteristic of magnets' composition and shape, with a coercive field of 60 G is observed at room temperature (Fig. 2). The strong magnetic behavior is readily observed by its being attracted to a permanent magnet at room temperature (Fig. 3). Thus, **1a** is the first example of organic-based material with a critical temperature exceeding room temperature. The critical temperature exceeds 350 K, the thermal decomposition temperature of the sample, and a linear extrapolation to the

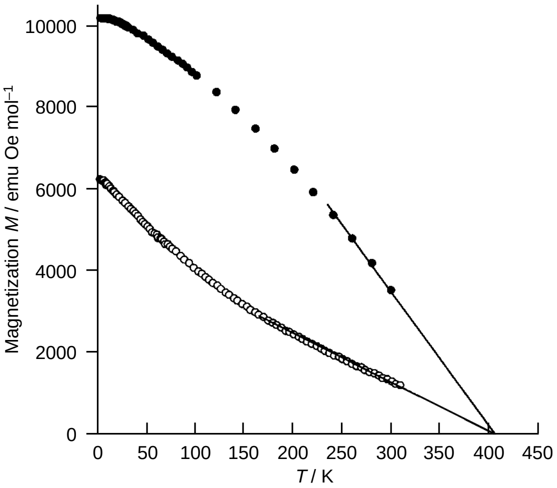


Fig. 1 Magnetization as a function of temperature [$M(T)$] at 1 kG for V(TCNE)$_x\cdot y$(CH$_2$Cl$_2$) prepared from (○) V(C$_6$H$_6$)$_2$ **1a**[7] and (●) V(CO)$_6$ **1b**[8]

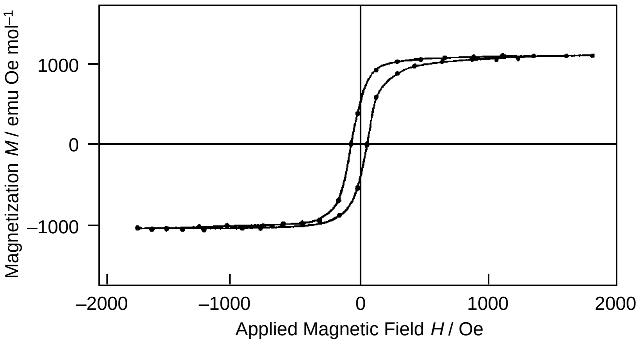


Fig. 2 Hysteresis $M(H)$, of $V(TCNE)_x{\cdot}y(CH_2Cl_2)$ **1a**, at room temperature

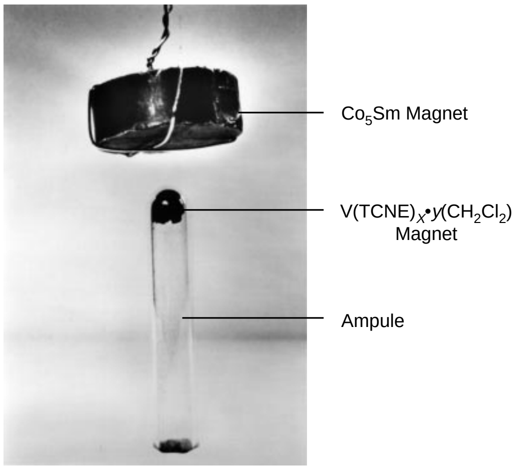


Fig. 3 Photograph of a powdered sample of **1a** being attracted to a Co_5Sm magnet at room temperature

temperature at which the magnetization should vanish leads to an estimate of T_c ~ 400 K (Fig. 1). Compound **1a** is also a semiconductor with a room temperature conductivity of ~10^{-3} S cm^{-1} which decreases with decreasing temperature. At low temperatures the conductivity becomes frequency dependent, suggesting a hopping conduction mechanism.[7d]

Thermal treatment of **1a** reduces the magnetization. At room temperature **1a** has a *ca.* 50 day half-life. Sealed samples heated for 10 h at 100 °C are significantly less magnetic, while heating to 160 °C for 48 h destroys magnetic ordering; however, the number of spins remains essentially unchanged. Concomitantly, the infrared spectra in the ν_{CN} region are altered slightly with the absorption at 2195 cm^{-1} moving to higher energy at 2206 cm^{-1}. Air exposure further alters the infrared spectra, with the major absorption in the $\nu_{C\equiv N}$ region shifting to 2220 cm^{-1}. Likewise, **1a** rapidly decomposes in air and looses magnetic ordering. Infrared analysis of the decomposed product has much weaker absorptions at 2225 cm^{-1} which is in the region reported for $TCNE^0$ [9] as well as TCNE π-bonds to metals atoms or ions.[10]

The reaction of $V(C_6H_6)_2$ and other strong acceptors such as TCNQ, perfluoro-TCNQ ($TCNQF_4$), $C_4(CN)_6$, 2,3,5,6-tetrachlorobenzoquinone (chloranil), 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and 2,3,5,6-tetracyanobenzoquinone (cyanil)[11] led to insoluble precipitates of unknown composition. These materials do not exhibit field-dependent magnetic susceptibilities and their high temperature susceptibilities can be fitted to the Curie–Weiss expression with $\theta < 0$ characteristic of antiferromagnetic, not ferromagnetic, behavior. Hence, magnets of nominal $V(\text{acceptor})_x{\cdot}y(\text{solvent})$ composition based on strong acceptors other than TCNE have yet to be prepared.

Compound **1a** is a structurally disordered material; hence, improved preparative routes leading to less disorder as well as avoiding the difficult-to-obtain $V(C_6H_6)_2$ were sought. Unlike $V^0(C_6H_6)_2$, the reaction of isoelectronic $V^0(C_5H_5)(C_7H_7)$ with TCNE did not afford a room-temperature magnet.[8] This is due to the greater oxidation potential of $V^0(C_5H_5)(C_7H_7)$ (0.34 V *vs.* SCE) with respect to $V^0(C_6H_6)_2$ (−0.28 V). Similarly, the reactions of $[TCNE]^{\cdot-}$ and $[V^I(C_6H_6)_2]^+$ or TCNE and $V^{II}(C_5H_5)_2$ did not afford a room-temperature magnet. Since the reaction of $V^0(C_6H_6)_2$ and TCNE leads to a strongly magnetic material, but the reaction of $[V^I(C_6H_6)_2]^+$ and $[TCNE]^{\cdot-}$ does not, the mechanism of the reaction is crucial in the formation of the room-temperature magnet and it is presently being investigated. In contrast, the room-temperature reactions of $V^0(CO)_6$, $[V^I(C_6H_6)_2][V^{-I}(CO)_6]$, $[V^{II}(NCMe)_6][V^{-I}(CO)_6]_2$, $[V^{II}(NCMe)_6]^{2+}$ and $[V^{II}(THF)_6][V^{-I}(CO)_6]_2$ with TCNE led to room-temperature magnets; while the reactions of $[Et_4N][V^{-I}(CO)_6]$ and $Na[V^{-I}(CO)_6]{\cdot}2$diglyme did not.[8] The reaction of $V^0(CO)_6$ with TCNE was studied in detail.[8]

The elemental composition suggests that the magnets prepared from $V(C_6H_6)_2$ or $V(CO)_6$ have similar compositions. The similarity of the IR spectra for the magnets prepared from $V(C_6H_6)_2$ (*i.e.* **1a**) and $V(CO)_6$ (*i.e.* **1b**) and the absence of $\nu_{C\equiv O}$ stretches in the 1800 to 2000 cm^{-1} region for the latter magnet strongly suggest that all the carbonyls are expelled from the vanadium coordination sphere upon the reaction of $V(CO)_6$ with TCNE.[8] This was confirmed from the quantification of CO-loss *via* Toepler pump measurements for [eqn. (1)],

$$V(CO)_6 + y\ \mathrm{TCNE} \longrightarrow V(TCNE)_y(CO)_{6-x}\ (\mathbf{1b}) + x\ CO \quad (1)$$

with $x = 5.9 \pm 0.1$. Thus, all the six carbonyls are lost. Based on the lack of CO and the similarity between the IR spectra for the magnets prepared from $V(CO)_6$ (**1b**) and $V(C_6H_6)_2$ (**1a**), both are assigned the same structural building block **2**. Nonetheless, differences between the ν_{CN} absorptions for **1a** and **1b** indicate that the two magnets are structurally inequivalent and different magnetic behavior is observed, although both have a T_c 400 K (Fig. 1).

The M for **1b** (Fig. 1), is 10 300 emu Oe mol^{-1} at 4.2 K and 3600 emu Oe mol^{-1} at room temperature and an applied magnetic field of 1 kG; an increase of 67 and 133% at these temperatures, respectively, as compared to **1a**. Whereas M decreases monotonically with increasing T for **1a**, this is less evident at low temperatures for **1b**. The unusual linear decrease of M with increasing T is consistent with extensive disorder in the sample, and suggests that the **1b** is less disordered. Hysteresis with a coercive field of 15 Oe is observed at room temperature and at 4.2 K for the **1b**. This is significantly lower than the 60 Oe value observed for **1a** (Fig. 2).[7] The extrapolated T_c for **1b** is ~400 K, comparable to **1a** (Fig. 1).[7] The results of the magnetic behavior for **1** give hope that more molecular/organic/polymeric magnets with higher T_cs will be available in the future. Already a room temperature a Prussian blue-structured magnet, also based on vanadium, has been reported.[12]

In addition to forming **1** *via* the solution reaction of TCNE and $V(C_6H_6)_2$ or $V(CO)_6$, these reactions were also carried out without solvent. No reaction occurred upon the reaction of TCNE and $V(C_6H_6)_2$, while an immediate blue precipitate occurred with TCNE and $V(CO)_6$ at the surface of the TCNE crystals or on the walls of the reaction vessel if both TCNE to $V(CO)_6$ were co-sublimed. For the latter product, the IR spectrum and magnetic properties were very similar to materials prepared from solution. However, this material has reduced oxygen sensitivity. This difference is attributed to its much lower surface area when compared to the fine (~100 m^2 g^{-1}) powders that are formed from solution.[13]

Due to T_c exceeding room temperature, applications for this magnet can be envisioned.[14] One application is for magnetic shielding, the attenuation of magnetic fields found in many electronic applications, *e.g.* high voltage lines. The feasibility of using **1** for this applications has been demonstrated (Fig. 4).[15]

Synthesis of the $V(TCNE)_x{\cdot}y(\text{solvent})$ magnet using solvents other than CH_2Cl_2 results in similar materials with varying

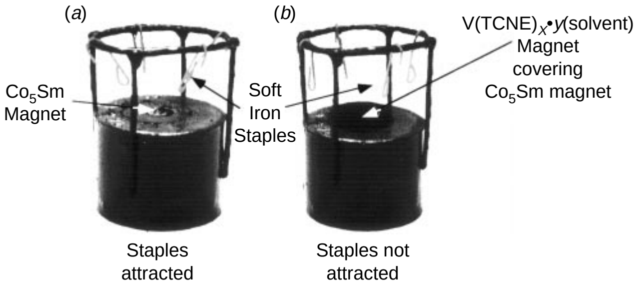


Fig. 4 Illustration of the V(TCNE)$_x$·y(CH$_2$Cl$_2$) magnet being an effective magnetic shield at room temperature; rods (paper clips) of soft-iron are attracted to a Co$_5$Sm permanent magnet (*a*); however, when a 1.7 mm pellet of V(TCNE)$_x$·y(CH$_2$Cl$_2$) is placed between the Co$_5$Sm magnet and the rods they hang freely (*b*) demonstrating magnetic shielding

degrees of structural order. For example, there is increasing disorder in the structure as the CH$_2$Cl$_2$ is replaced by THF[7b] (T_c ~ 210 K) and MeCN[7c] (T_c ~ 100 K). The exact magnetic ordering temperature varies with preparation conditions and resulting structural order. With increasing order these materials show features of correlated spin glass behavior. Additional examples of this class of magnets are needed to understand the chemistry and physics.[7,8] To date the reaction of V(C$_6$H$_6$)$_2$ or V(CO)$_6$ with other strong acceptors does not form magnetically ordered materials. Attempts to replace V with Cr, *i.e.* the reaction of TCNE with Cr(C$_6$H$_6$)$_2$ or Cr(CO)$_6$, lead to nonmagnetically ordered, but ferromagnetically coupled, [Cr(C$_6$H$_6$)$_2$][TCNE][16] and a substitution reaction with Cr(CO)$_6$ forming Cr(CO)$_5$(TCNE).[17] However, magnets of M(TCNE)$_2$·y(solvent) stoichiometry have recently been reported.

M(TCNE)$_2$·y(CH$_2$Cl$_2$) (M = Mn, Fe, Co, Ni) have been prepared *via* the reaction of MI$_2$·xMeCN in CH$_2$Cl$_2$.[18] The ν_{CN} absorption bands for M(TCNE)$_2$·xCH$_2$Cl$_2$ are consistent with coordinated [TCNE]$^{\cdot -}$ and are similar, albeit sharper and occur at higher in energy, to that observed for V(TCNE)$_x$·y(CH$_2$Cl$_2$). In contrast to disordered V(TCNE)$_x$·y(CH$_2$Cl$_2$), M(TCNE)$_2$·xCH$_2$Cl$_2$ (M = Mn, Fe) give X-ray powder patterns, which have yet to be indexed.

The spin and oxidation states of Fe(TCNE)$_2$·xCH$_2$Cl$_2$ **3** were determined from ^{57}Fe Mössbauer spectroscopy.[18] Above 95 K, **3** has absorptions with large chemical shift [δ = 1.23 mm s^{-1}] and quadrupole coupling [ΔE_q = 3.26 mm s^{-1}] characteristic of hexacoordinate, high-spin Fe^{II} compounds[19] (Fig. 5). Below 95 K, the spectra become more complex due to magnetic splitting [δ = 1.24 mm s^{-1}; ΔE_q = 3.31 mm s^{-1}, H_{int} = 229 KOe] (Fig. 5) in agreement with the critical temperature determined *via* magnetic studies (*vide infra*).

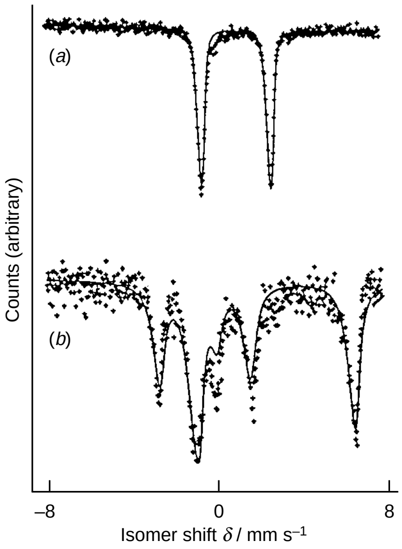


Fig. 5 ^{57}Fe Mössbauer spectra of Fe(TCNE)$_2$·xCH$_2$Cl$_2$ at (*a*) 50 and (*b*) 100 K[18]

Complex **3** has a complex magnetic behavior which is essentially independent of preparation and amount of solvent.[18] The susceptibility cannot be fitted to the Curie–Weiss law, $\chi \propto (T - \theta)^{-1}$, as expected for high-spin d^6 Fe^{II} in an octahedral environment with spin-orbit coupling. A spontaneous magnetization occurs below a T_c of 121 K, taken here as the intercept with the temperature axis of the initial slope of the magnetization as a function of temperature (Fig. 6). At 2 K the magnetization shows a complex, poorly understood response to the field, reminiscent of metamagnetic behavior. At 5 T and 2 K the observed magnetization is *ca.* 16 900 emu Oe mol^{-1}; however, higher fields are necessary to achieve saturation. This value of saturation magnetization corresponds to three S = 1/2 spins and exceeds the comparable value of 10 300 emu Oe mol^{-1} for V(TCNE)$_x$·y(CH$_2$Cl$_2$) prepared from V(CO)$_6$[8] by 63%, as well as exceeding the expectation of that from antiferromagnetically coupling between an S = 2 Fe^{II} site and two S = 1/2 [TCNE]$^{\cdot -}$, *i.e.* 11 200 emu Oe mol^{-1}, but is substantially less than the expectation from ferromagnetic coupling, *i.e.* 33,500 emu Oe mol^{-1}. Although the T_c shows little dependence on the synthetic route, hysteresis loops taken at 2 K show a strong variation in the coercive field ranging from 300 to 3000 G. Likewise, the detailed field and zero field cooled curves also have a strong dependency on reaction conditions and aging.

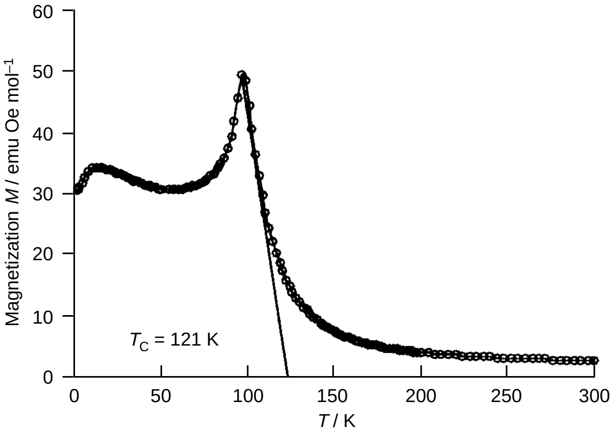


Fig. 6 Zero-field cooled magnetization as function of temperature for Fe(TCNE)$_2$·0.75CH$_2$Cl$_2$

Fe(TCNE)$_2$·xCH$_2$Cl$_2$ shows remarkable thermal stability. The IR spectrum and X-ray powder pattern, as well as magnetic data of a sample heated at 130 °C for 38 h, suggest that the chemical and structural features of the materials are preserved after the heat treatment, except for the apparent solvent loss. Some thermal degradation is observed from magnetic measurements on a sample treated at 180 °C, and massive decomposition is evident from IR studies when the material is heated to 200 °C. TGA data show that although desolvation starts at temperatures as low as 40 °C, it does not approach completion until the sample decomposes. Since CH$_2$Cl$_2$ is a poorly coordinating solvent, the high desolvation temperature may be attributed to CH$_2$Cl$_2$ being trapped into a three-dimensional network, and is only completely released when the structure collapses. Fe(TCNE)$_2$·xCH$_2$Cl$_2$ is not pyrophoric as is V(TCNE)$_x$·y(solvent), but it does decompose in air.

Reactions of TCNE and MeCN solvates of MI$_2$ (M = Mn, Co, Ni) led to M(TCNE)$_2$·xCH$_2$Cl$_2$ species which magnetically order with T_c values of 44 (M = Ni, Co) and 107 K (M = Mn)[8] (Table 1). The nearest neighbor spin coupling energy, J, can be estimated from the mean-field expression of $T_c = JzS(S + 1)/3k_B$, where k_B = Boltzmann's constant, z = number of nearest neighbors, *i.e.* 6, and assuming $H = -2JS_a \cdot S_b$. The

Table 1 Summary of the infrared ν_{CN} absorption bands, saturation magnetization M_s, ordering temperature T_c and exchange energy J for M(TCNE)$_2$·xCH$_2$Cl$_2$ (M = V, Mn, Fe, Co, Ni)[18]

Metal	Saturation magnetization[a] M_s/ emu Oe mol^{-1}	T_c/K	J/K[b]
V[c]	10 300	~ 400	53
Mn[d]	19 000	107	6.1
Fe[d]	16 900	121	10
Co[d]	8 000	44	5.9
Ni[d]	15 800	44	11

[a] 2 K and 5 T. [b] See text. [c] Ref. 7. [d] Ref. 18.

resulting estimates of J ranges as V ≫ Ni ~ Fe > Mn ~ Co (Table 1). Mn(TCNE)$_2$·xCH$_2$Cl$_2$ is isostructural to Fe(TCNE)$_2$·xCH$_2$Cl$_2$ based upon powder diffraction data; however, for M = Ni, Co the solids diffract poorly and do not appear to be isomorphous to M(TCNE)$_2$·xCH$_2$Cl$_2$ (M = Fe, Mn). Hence, based upon the composition and the similarity of the ν_{CN} absorptions for M = Mn, Co and Ni, we assign all the metals as being divalent. Likewise, the elusive oxidation state of V in the room temperature V(TCNE)$_x$·yCH$_2$Cl$_2$ magnet is again assigned the divalent oxidation state.[7,8]

Hysteresis is observed for all the magnets below T_c, however, as observed for V(TCNE)$_x$·y(CH$_2$Cl$_2$),[7,8] the coercive field varies from preparation to preparation. Nonetheless, the observed coercive fields range from 50 (M = Ni) to 6500 Oe (M = Co). The shape of the hysteresis curves is characteristic of metamagnetic behavior in some cases, *e.g.* for Fe(TCNE)$_2$·0.75CH$_2$Cl$_2$ at 2 K (Fig. 7) and, along with more detailed magnetic studies, including ac measurements, is the focus of future research.

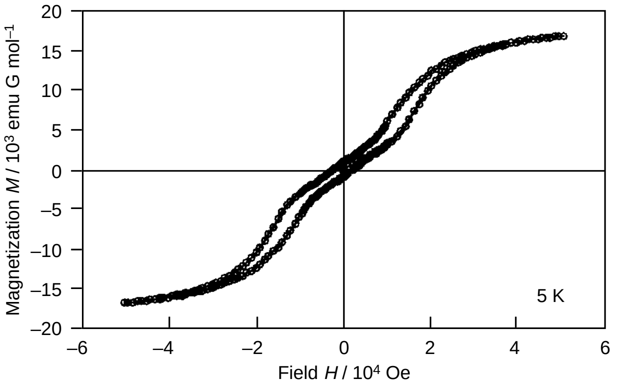
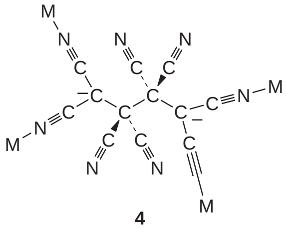


Fig. 7 An example of the observed hysteretic $M(H)$ for Fe(TCNE)$_2$·0.75CH$_2$Cl$_2$ at 2 K. The observed coercive field for this sample is 2300 Oe and the sample saturates to 16 900 emu Oe mol^{-1}.

Hence, a new synthetic route enabling the preparation of several new examples of molecule-based magnets of M^{II}(TCNE)$_2$·xCH$_2$Cl$_2$ composition has been identified. These new magnets have T_c values that exceed 100 K and coercive fields as great as 6500 Oe.

While preparing the M^{II}(TCNE)$_2$·xCH$_2$Cl$_2$ magnets, crystals (light yellow for M = Mn; dark brown for M = Fe) which did not magnetically order were isolated. Single crystal X-ray diffraction studies revealed the unprecedented octacyanobutanediide dianion, [C$_4$(CN)$_8$]$^{2-}$ **4**, bound to four octahedral M^{II}s in a plane with the MeCN molecules filling the axial coordination sites, *i.e.* Mn[C$_4$(CN)$_8$](NCMe)$_2$·CH$_2$Cl$_2$ **5** and Fe[C$_4$(CN)$_8$](NCMe)$_2$·MeCN **6**.[20] Compound **4** is disordered about the midpoint of the central C–C bond for M = Mn, but is ordered for M = Fe, and has long 1.59 (2) (M = Mn) and 1.627 (14) Å (M = Fe) central C–C bonds suggesting that it is a weak bond. This is the first example of a σ-dimer of [TCNE]$^{\cdot-}$, however, several examples of a structurally related σ-dimer of [TCNQ]$^{\cdot-}$ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane) have been reported.[21]



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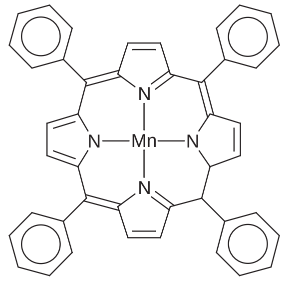
Compounds **5** and **6** are paramagnets obeying the Curie–Weiss law above 5 K. This is consistent with diamagnetic [C$_4$(CN)$_8$]$^{2-}$ weakly coupling the metal spin sites (S = 5/2 Mn^{II}). Upon desolvation of **5** and **6** at 100 °C the ν_{CN} IR absorptions disappear and new ν_{CN} bands characteristic of the M(TCNE)$_2$·xS magnets[20] (M = Mn, Fe) appear. Desolvated **5** magnetically orders at a T_c of 95 K,[20] in reasonable agreement with samples prepared from CH$_2$Cl$_2$.[18] Compound **6** behaves in a similar fashion upon desolvation. These observations suggest that upon desolvation the S = 0 μ$_4$-[C$_4$(CN)$_8$]$^{2-}$ reforms two S = 1/2 [TCNE]$^{\cdot-}$ units which can bind to additional metal centers, providing stronger spin coupling leading to the observed magnetic ordering. Evidence for this type of bond breaking has been reported for σ-dimers of [TCNQ]$^{\cdot-}$.[21a]

Hence, additional members of the M(TCNE)$_x$ class of magnets have been characterized, and in the case of Fe the metal is assigned to be divalent as previously proposed for V(TCNE)$_x$·$y$solvent.[7] Furthermore, an intermediate in the formation of the M(TCNE)$_x$ class of magnets, namely [C$_4$(CN)$_8$]$^{2-}$ **6**, has been identified and structurally characterized.

[Mn(porphyrin)][TCNE]-based magnets

Another class of TCNE-based magnets is exemplified by [Mn^{III}TPP]$^+$[TCNE]$^{\cdot-}$ (TPP = *meso*-tetraphenylporphinato), which forms a coordination polymer (1-D) that was characterized to be a ferrimagnet with T_c 14 K.[22] With the goal of identifying the importance of 1-D with respect to 3-D interactions and developing a structure–function relationship for this class of magnetic materials, as well as preparing new molecule-based magnets with enhanced T_cs, we have pursued the study of this class of compounds.



MnTPP

[Mn^{III}TPP]$^+$[TCNE]$^{\cdot-}$ forms uniform parallel 1-D chains in the solid state with each S = 2 Mn^{III} bonded to four porphyrin nitrogens (*ca.* 2.00 Å) and axially to two [TCNE]$^{\cdot-}$ nitrogens (*ca.* 2.30 Å), and each S = 1/2 [TCNE]$^{\cdot-}$ is *trans*-μ-bonded to two Mn^{III} species, [Fig. 8 (*a*)]. The magnetic susceptibility of [MnTPP]$^+$[TCNE]$^{\cdot-}$·2PhMe can be fitted to the Curie–Weiss expression above 280 K with θ ~ −15 K, and between 115 and 250 K with an effective θ, θ', of +61 K. A minimum in the value of χT, characteristic of 1-D ferrimagnetic behavior, is observed at ~ 310 K and field-dependent susceptibility is observed below 50 K. Magnetic ordering occurs below 13 K (as determined by scaling analysis[22c]) and hysteresis with a coercive field of 375 G was obtained at 5 K.[22] Thus, [MnTPP][TCNE] is a representative example of a new structure type of organic-based magnetic materials, and is an excellent model system for

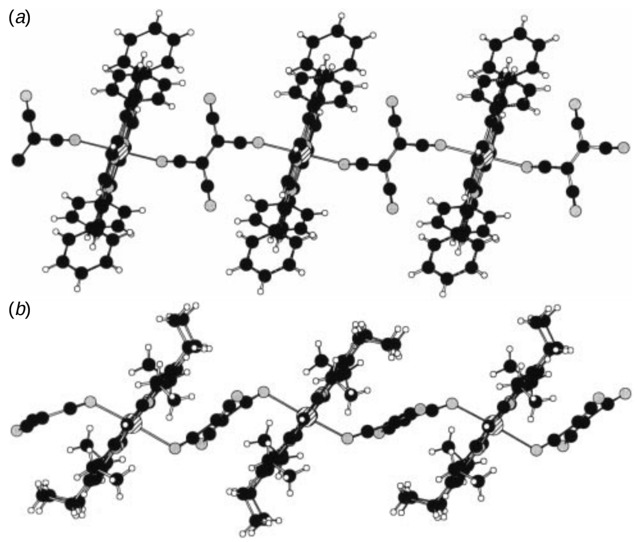


Fig. 8 (*a*) Segment of a uniform chain of the ferrimagnetic [Mn^{III}TPP][TCNE]·2PhMe coordination polymer (the solvent is omitted for clarity). (*b*) Alternating chain segment of the paramagnetic [Mn^{III}OEP][TCNE] coordination polymer.

studying a number of unusual magnetic phenomena, for example, the magnetic behavior of mixed quantum/classical spin systems.

In addition to modification of the porphyrin ring, the clathrate nature of this class of metalloporphryins[23] enables the introduction of different solvents into the structure to alter the inter- and intra-chain couplings and the magnetic properties. In this review we focus on modification of the [MnTPP][TCNE] structure type and discuss the consequent magnetic properties.

[MnTPP][TCNE]·2PhMe **6**[22*a*] has been crystallographically characterized. Likewise, the [TCNE]$^{\cdot-}$ salts of 4-methoxyphenyl (**7**),[24] 4-chlorophenyl (**8**)[25] and 2-fluorophenyl substituted [MnTPP]$^+$ (**9**)[24] and *meso*-tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphinatomanganese(III), MnTP′P[26] (**10**), have been studied by single crystal X-ray diffraction. Furthermore, to extend this system the analogous TCNE electron-transfer salt was prepared with the easier-to-oxidize MnOEP (OEP = octaethylporphyrinato).[27]

[MnOEP][TCNE] has weak ferromagnetic coupling as evidenced by the fitting of the susceptibility to the Curie–Weiss expression with a θ' of +7 K.[27] However, unlike [MnOEP][TCNE], magnetic ordering is not observed above 2 K. The differences in the magnetic properties are ascribed to structural differences. Although both [MnTPP][TCNE]·2PhMe and [MnOEP][TCNE] form parallel 1-D chains (Fig. 8), due to the differing orientations of [TCNE]$^{\cdot-}$ within a chain they are alternating chains for [MnOEP][TCNE] instead of being uniform chains as for [MnTPP][TCNE]·2PhMe. Thus, uniform chains appear to be important to achieve long range magnetic order.[27]

A correlation of the dihedral angle, ϕ, between the [Mn^{III}TPP]$^+$ MnN$_4$ and [TCNE]$^{\cdot-}$ mean planes and the magnitude of magnetic coupling has been observed for ditoluene solvates of five [TCNE]$^{\cdot-}$ salts, **6–10**.[28] The magnitude of magnetic coupling is determined from $T_{\min}$, the temperature at which a minimum in $\chi T(T)$ or $\mu(T)$ plots occurs, as expected for antiferromagnetically coupling linear chain systems,[29] and the effective θ, θ', obtained from a fit of the data to the Curie–Weiss expression. A correlation to $T_{\min}$ is preferred as it is model independent; however, for strongly coupled systems $T_{\min}$ is not observed as it occurs at temperatures exceeding the measurement range. $T_{\min}$, however, can be estimated from a fit of the data to the Seiden expression for isolated 1-D chains comprised of alternating quantum (S = 1/2) and classical (S > 1/2) spins.[30]

The smaller ϕ the stronger the magnetic coupling, *i.e.* the greater $T_{\min}$ and θ' (Fig. 9). Hence to attain strong intrachain coupling systems with more acute dihedral angles are sought and, based on **10**, 3,5-disubstituted [MnTPP]$^+$s are preferred over 2- or 4-substituted [MnTPP]$^+$s which from the data acquired to date have higher ϕ values. To test this postulate several 3,5-disubstituted systems are being studied. Likewise, pressure also may force such systems to have reduced angles and also lead to higher T_c values.

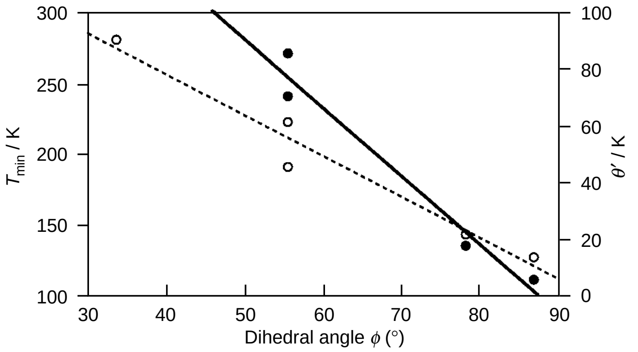


Fig. 9 Correlation of the dihedral angle ϕ between the MnN$_4$ and [TCNE]$^{\cdot-}$ mean planes with the temperature at which $\chi T(T)$ data has a minimum, ($T_{\min}$, ● and solid line) and the effective θ value (θ'; ○ and dashed line)[28]

The aforementioned correlation between ϕ and $T_{\min}$ and θ' is attributed to the overlap between the [TCNE]$^{\cdot-}$ *N*-bound to Mn^{III} π* SOMO and the four Mn^{III} SOMO d orbitals. [The energy of the latter increase as d_{xy^1} (b$_1$) < d_{xz^1}, d_{yz^1} (e) < $d_{z^2}{}^1$ (a$_1$) < $d_{x^2-y^2}$ (b$_1$).[31]] From MO considerations (determined from semi-empirical INDO/SCF calculations) the expected d_π–p_z (d_π = d_{xz}, d_{yz}) overlap is not as important as the σ–d_{z^2}/p_z overlap between Mn^{III} and the [TCNE]$^{\cdot-}$ (Fig. 10).[28] Furthermore, the smaller ϕ increases the σ–d_{z^2}/p_z overlap between Mn^{III} and the [TCNE]$^{\cdot-}$ leading to an increased intrachain coupling, as reflected in $T_{\min}$ and θ' (Fig. 10).

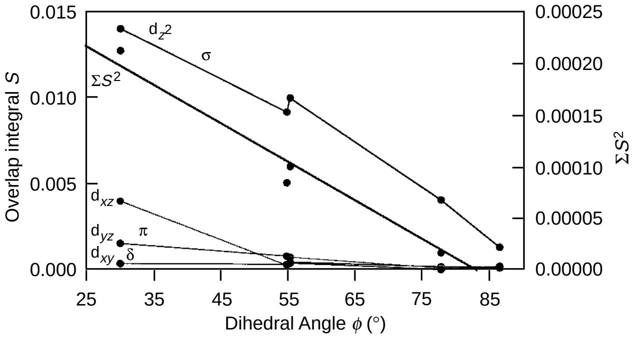


Fig. 10 Correlation of the dihedral angle ϕ between the MnN$_4$ and [TCNE]$^{\cdot-}$ mean planes with the semi-empirical INDO/SCF calculated d_{yz}-, d_{xz}-, d_{xy}- and d_{z^2}-like overlap integrals S with the [TCNE]$^{\cdot-}$ π* SOMO and the sum of the squares of these overlap integrals ΣS^2

While the σ overlap between the [TCNE]$^{\cdot-}$ p_z orbital and the Mn d_{z^2} orbital controls the intrachain magnetic exchange, the three-dimensional magnetic ordering temperature, T_c, depends upon this term *and* the interchain exchange. The later term is governed by the competition between antiferromagnetic exchange due to orbital overlap between porphyrin moieties of adjacent chains and an effective exchange due to dipolar interactions between chains. The dipolar term can be ferromagnetic or antiferromagnetic depending upon the structural order in the compound and the role of single ion anisotropy.[32]

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Table 2 Summary of the structural and magnetic parameters for the several [TCNE]$^{\cdot -}$ magnets

Porphyrin	Mn–N$_{\mathrm{TCNE}}$ distance/Å	Dihedral angle (°)	Mn$\cdots$Mn distance^{a}/Å	Effective θ/K	T_{min}/K
[MNnTPP][TCNE]·2PhMe	2.306	55.4	10.116	61	270
[MnTClPP][TCNE]·2PhMe	2.267	86.8	10.189	13	110
[MnTOMePP][TCNE]·2PhMe	2.289	78.1	10.256	21	134
[MnTFPP][TCNE]·2PhMe	2.313	55.4	10.185	45	240
[MnTP′P[TCNE]·2PhMe	2.299	33.6	8.587	90	$>300^{b}$

[a] Intrachain. [b] Not plotted in Fig. 10.

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